

# **Atmospheric Chemicals' Sources and Fates: Nonmethane Organic Compounds**

**Paul V. Doskey, Yoshiko Fukui, and Weigang Gao**

Atmospheric Section  
Environmental Research Division  
Argonne National Laboratory

## **Objectives**

- Investigate the effect of energy-related trace chemicals on the photochemistry of the atmosphere.
- Investigate the long-range transport of these substances and their transformation products over global scales.

## **Approach**

- Measurements of the horizontal and vertical distribution of nonmethane organic compounds above urban and rural areas
- Modeling efforts
- Instrument and method development

# Nonmethane Organic Compounds (NMOCs)

C<sub>1</sub>-C<sub>12</sub>

OxHCs (Oxygenated Hydrocarbons)

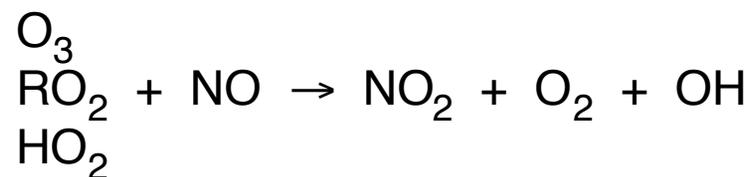
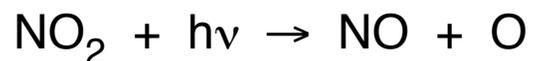
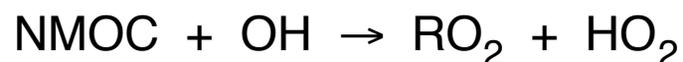
Alcohols, Aldehydes, Ketones, Ethers

NMHCs (Nonmethane Hydrocarbons)

Aliphatic and Aromatic Hydrocarbons

# Atmospheric Chemistry

The NMOCs are precursors to oxidant formation. They are oxidized by OH forming a complex mixture of peroxy radicals that oxidize NO to NO<sub>2</sub> without consuming O<sub>3</sub> and thus, allow O<sub>3</sub> to accumulate in the atmospheric boundary layer (ABL).



## Sources

On a global scale the emission rate of NMOCs from natural sources are nearly a factor of ten greater than the emission rate from anthropogenic sources. On a national scale the emission rates from the two source categories are nearly equal. Natural sources include emissions from deciduous, coniferous, and herbaceous vegetation, and also agricultural crops. Anthropogenic emissions are associated with the use, distribution, and refining of petroleum fuels.

---

Source	Emission Rate (Tg C yr <sup>-1</sup> )	
	Global	National
Natural	650	24
Anthropogenic	75	20

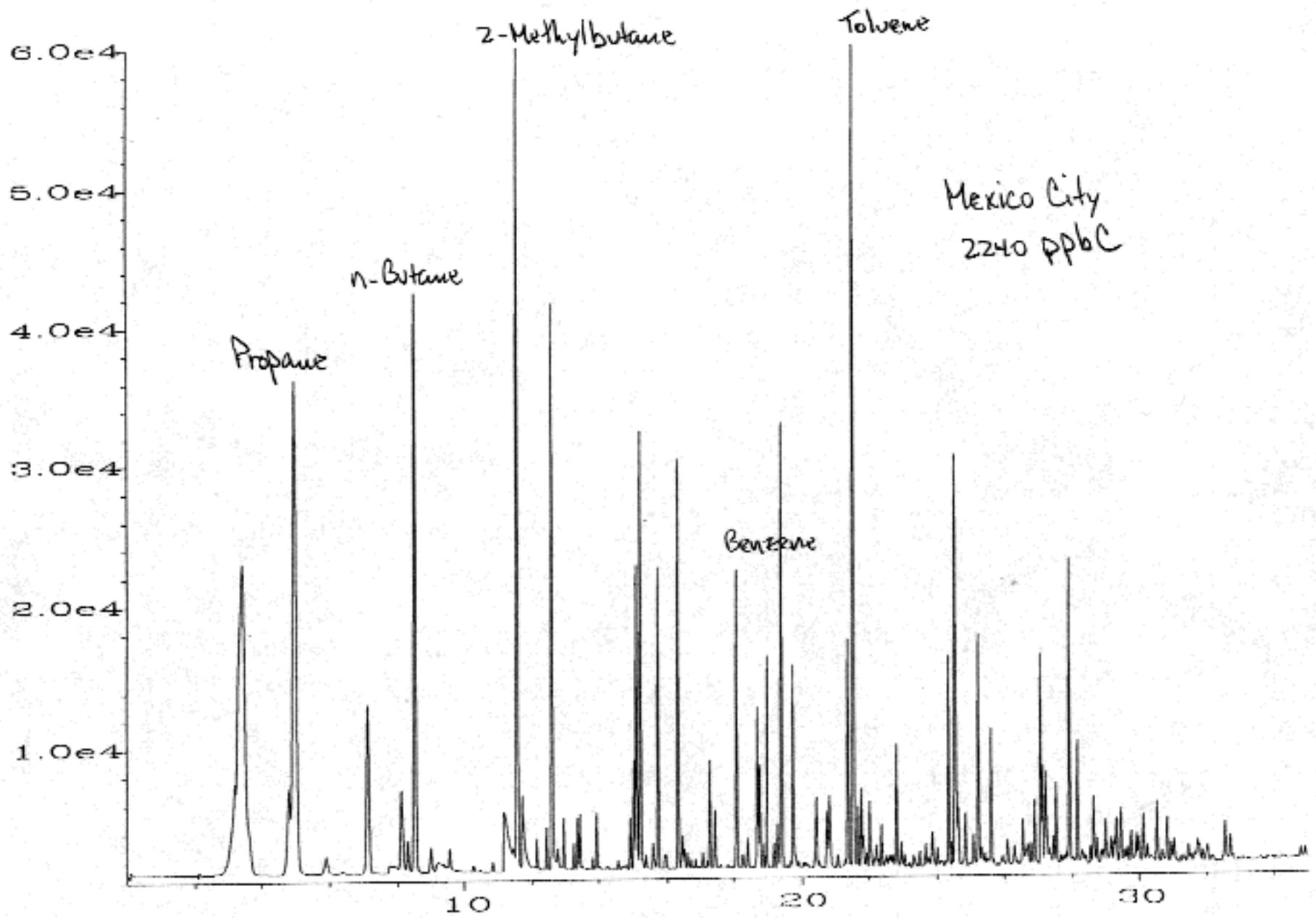
---

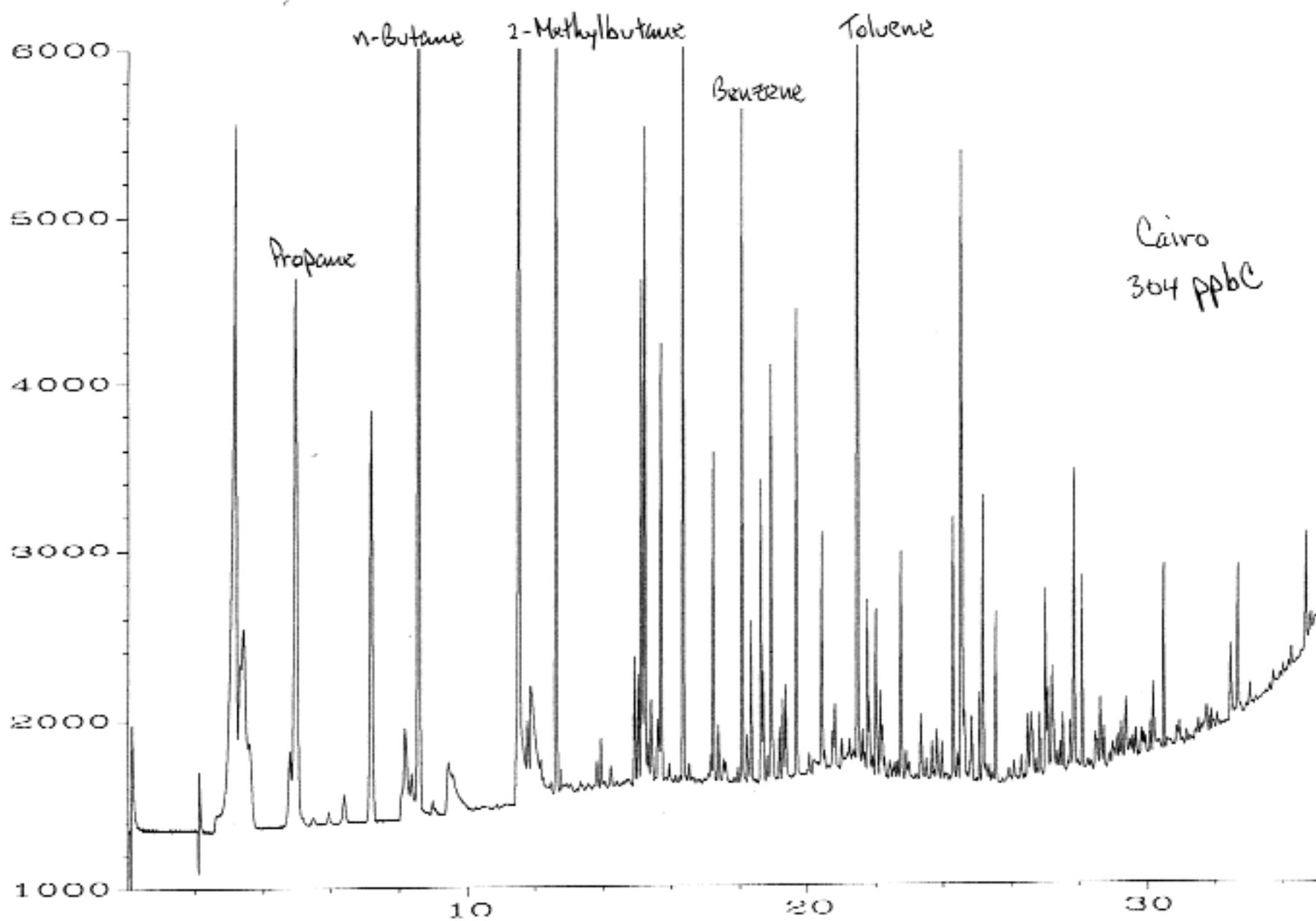
# Measurements

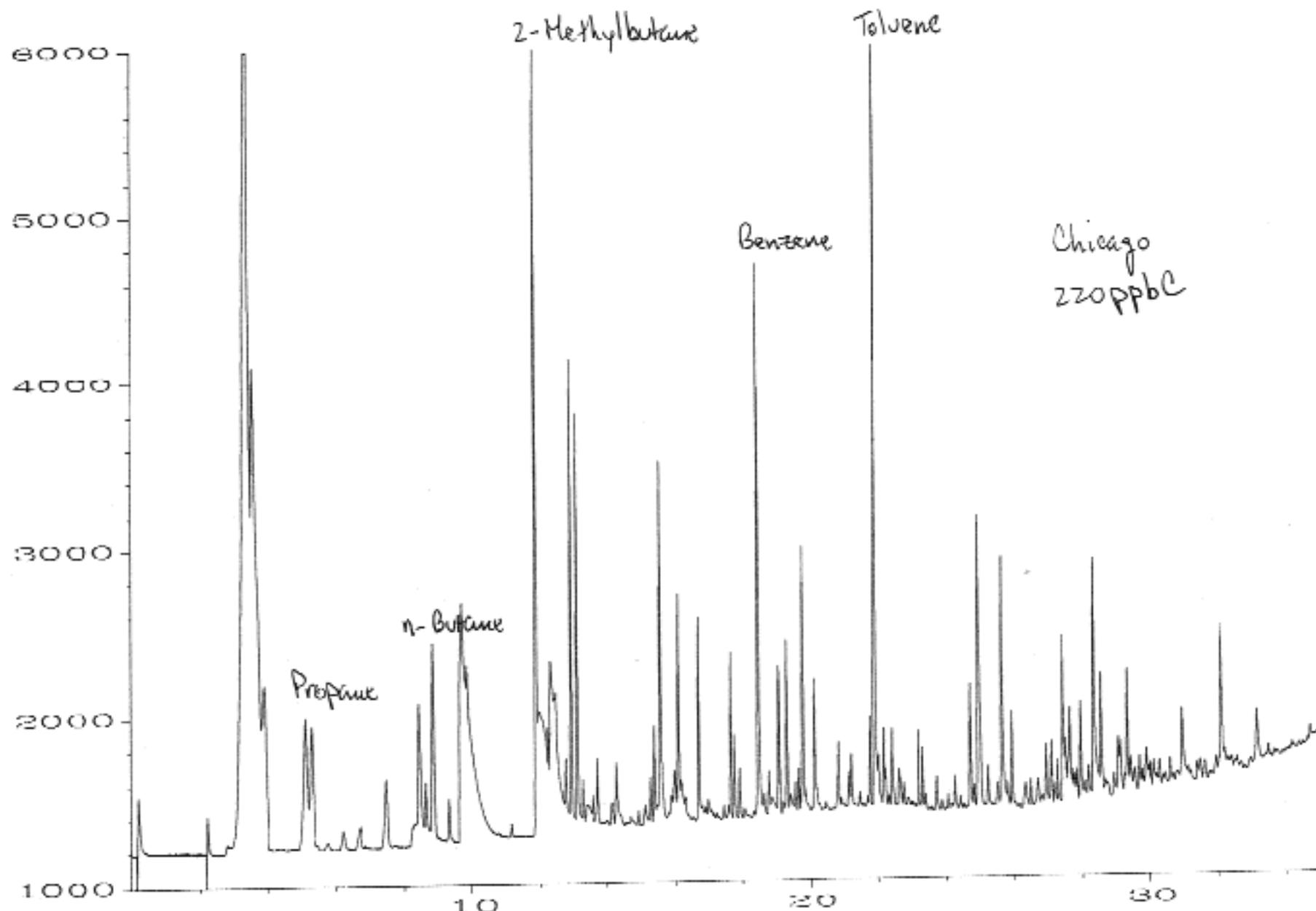
## Distributions in Ambient Air

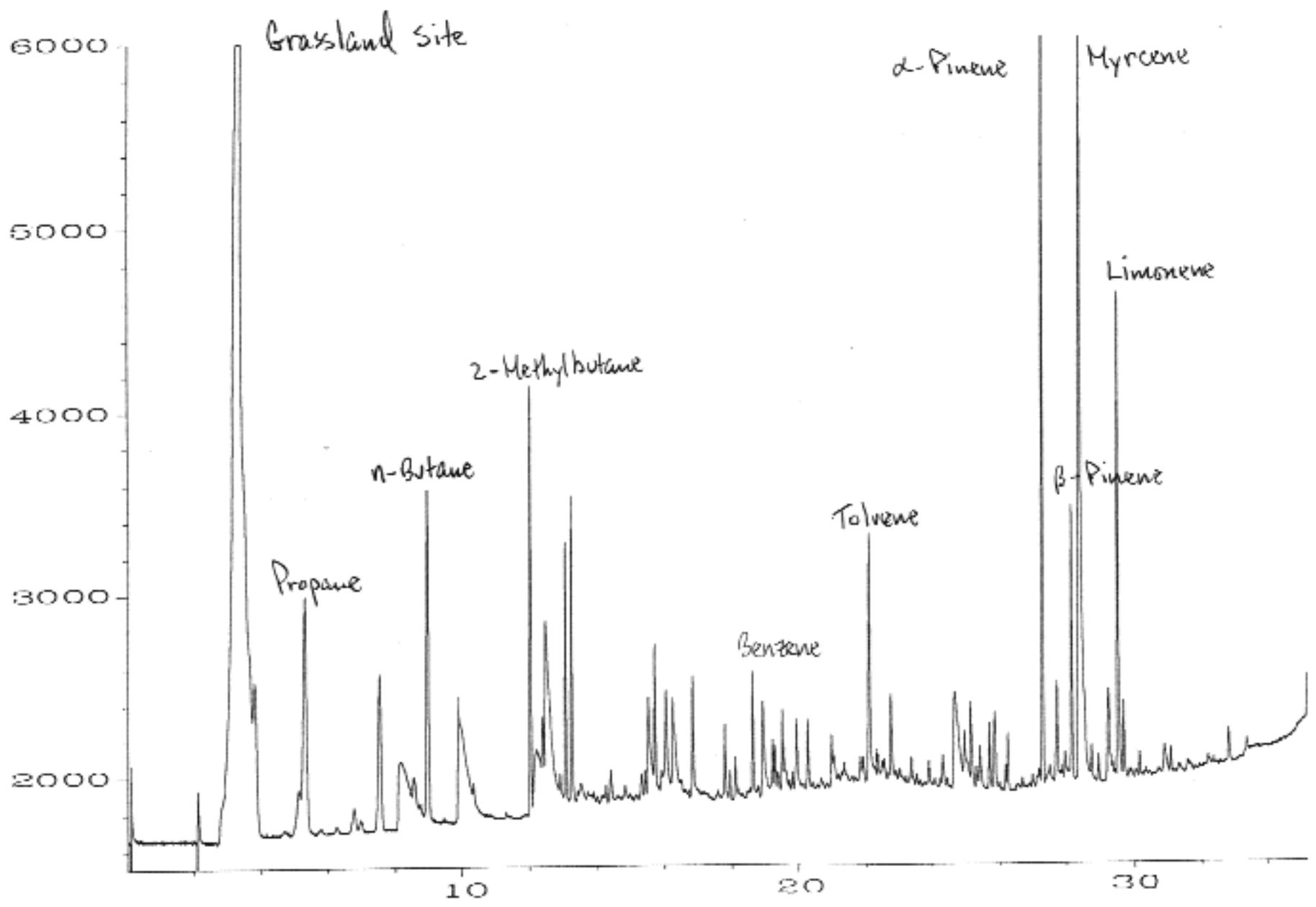
**Urban Air** - A large fraction of the NMOCs in urban air originates from vehicles and petroleum refineries, and fugitive emissions of petroleum fuels such as liquefied petroleum gas (LPG). Hydrocarbons typical of LPG **emissions** include **propane**, **n-butane**, and **2-methylbutane**. **Vehicle emissions** contain high concentrations of **benzene** and **toluene**. High-resolution gas chromatograms of ambient air samples collected in Mexico City, Mexico; Cairo, Egypt; and Chicago, Illinois contain a complex mixture of more than 150 hydrocarbons. Fugitive emissions of LPG in Mexico City and Cairo appear to be nearly equal in magnitude to the vehicle emissions. Although 2-methylbutane is present in urban Chicago, the source of this hydrocarbon is gasoline and not LPG because the LPG in the United States contains mostly propane.

**Rural Air**- The NMOC distribution in rural air is dominated by natural emissions from vegetation. The high-resolution gas chromatogram of ambient air collected at a grassland site in suburban Chicago exhibits a contribution by anthropogenic sources; however, emissions from **herbaceous vegetation** are also significant as indicated by the presence of several monoterpenes,  **$\alpha$ -pinene**,  **$\beta$ -pinene**, **myrcene**, and **limonene**.









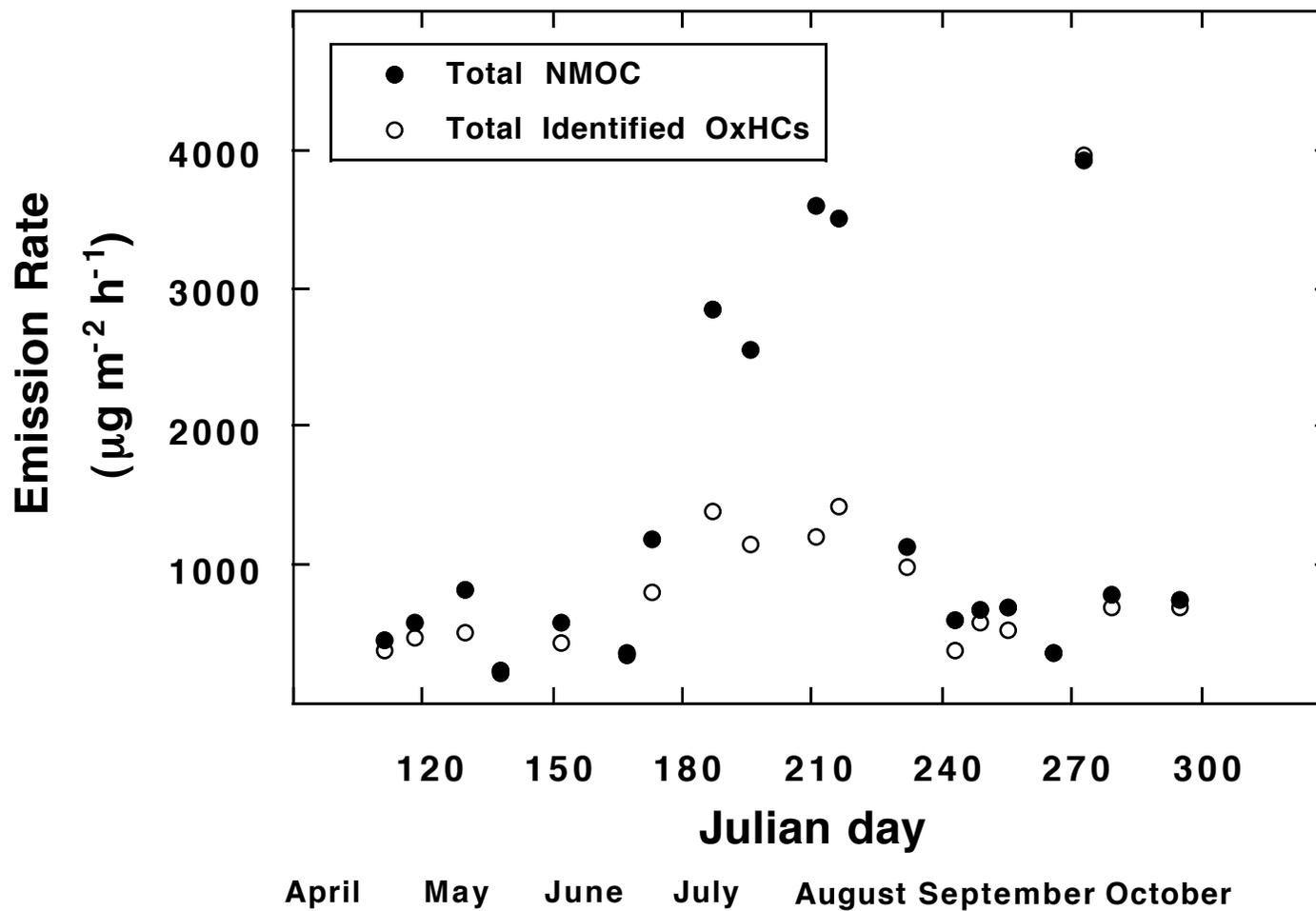
## Emissions from Natural Sources

The NMOC emissions from vegetation are composed of a complex mixture of NMHCs and OxHCs. The NMHCs include **isoprene**, which is emitted from deciduous trees, and **monoterpenes**, which originate from coniferous trees. **Methanol** is also emitted from deciduous trees at rates that approach those of isoprene. Monoterpenes and methanol, and many other OxHCs such as **cis-3-hexen-1-ol**, are also emitted from herbaceous vegetation.

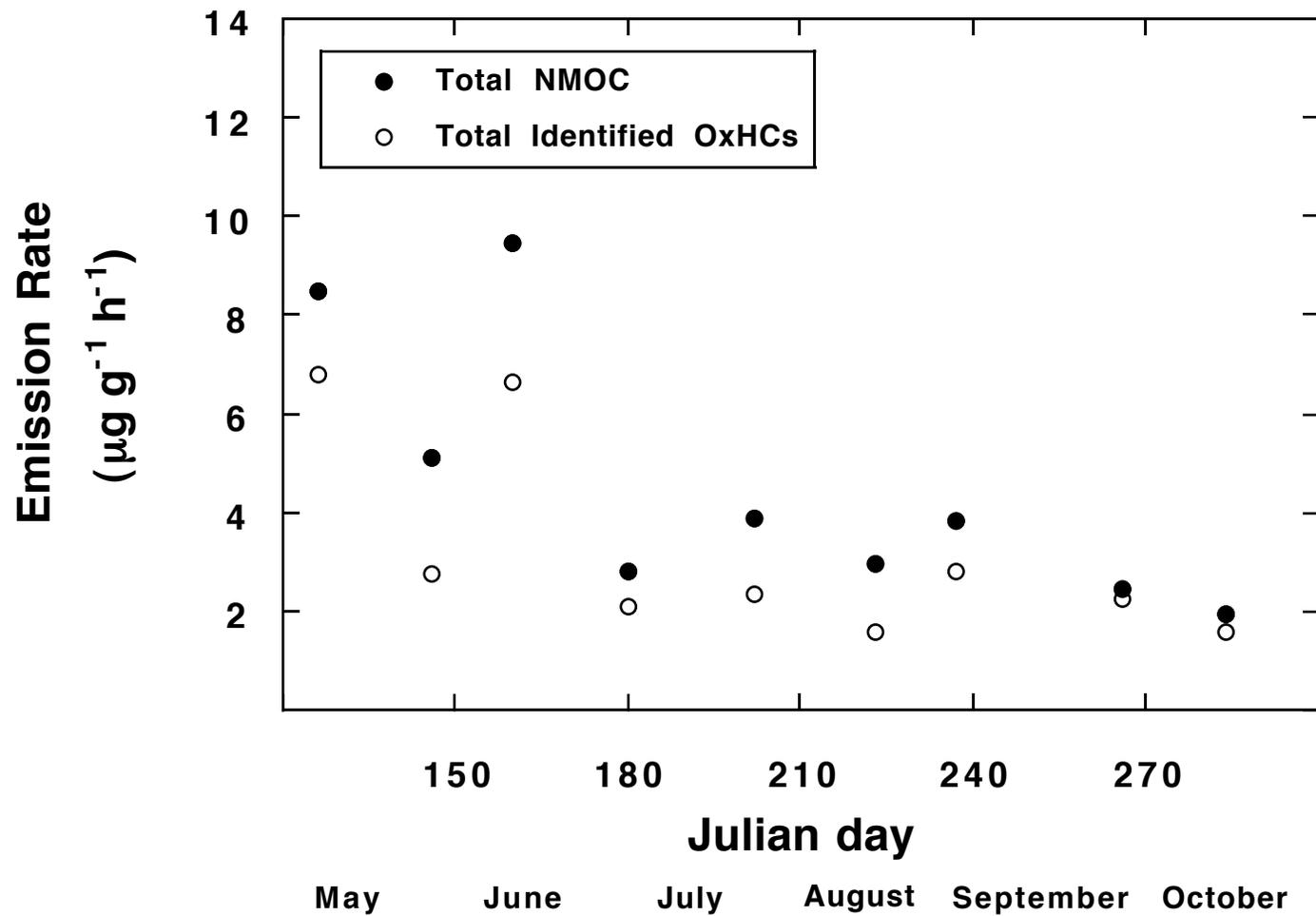
The NMOC emissions from grasslands exhibit a **seasonal variation** that is dependent on the **maturity of the vegetation** and growth stages such as **flowering**. Emissions of monoterpenes ( $\alpha$ - and  $\beta$ -pinene, limonene, and myrcene) and cis-3-hexen-1-ol were accelerated by a factor of 3-4 during the flowering of the plants. Year-to-year variations in the average emission rates varied by a factor of 2 and were related to the frequency and temporal profile of precipitation during the growing season, which had a direct effect on the viability of the vegetation.

The emission rates of some NMOCs, particularly **ethanol**, from grassland vegetation subjected to **hypoxia** and **frost** were a factor of 6 greater than the average emission rates.

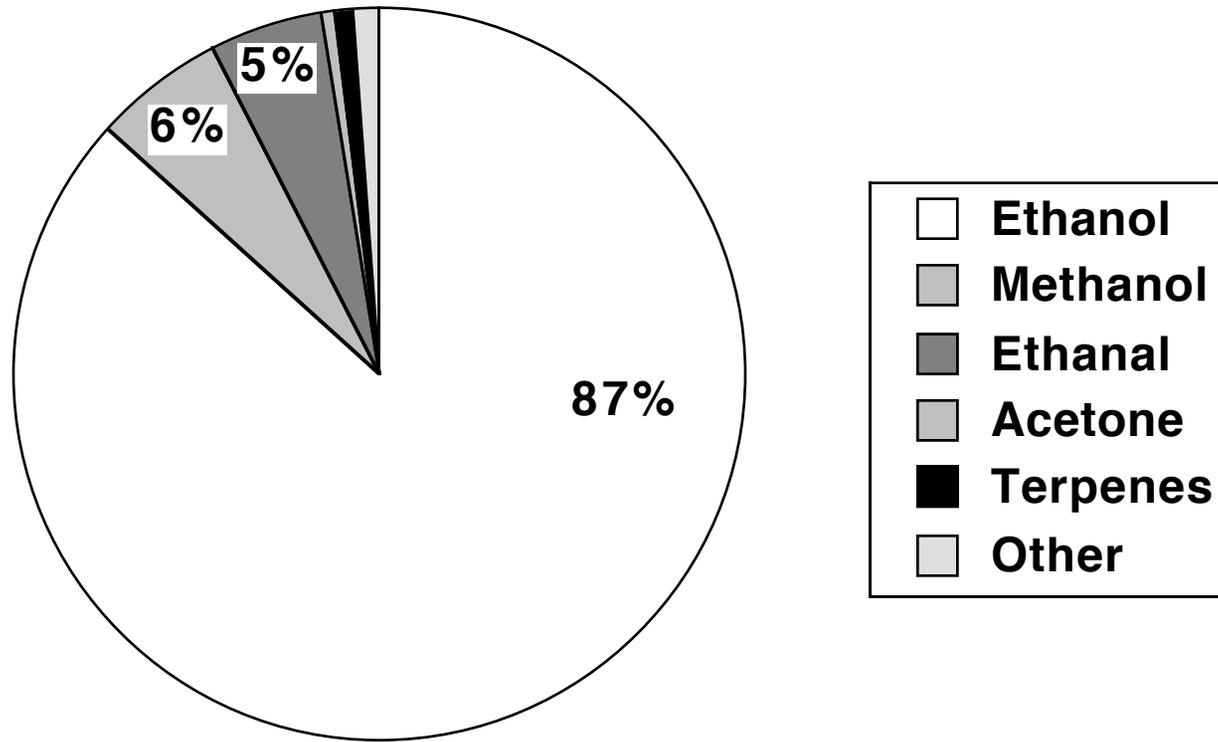
# Fixed Location



# Variable Locations



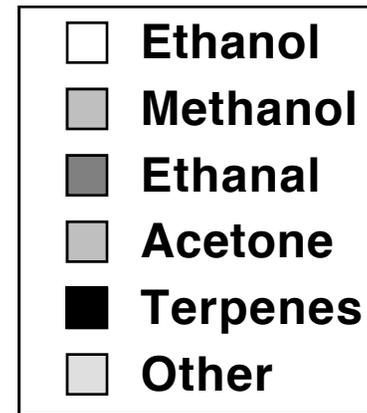
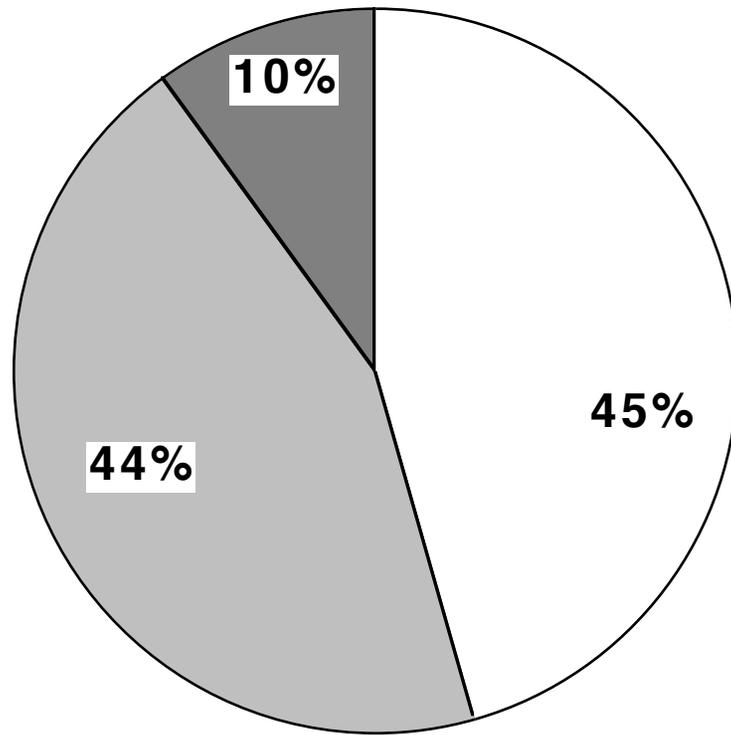
# Hypoxia



**Julian Day 160**

**10,500  $\mu\text{g m}^{-2} \text{h}^{-1}$**

# Frost



**Julian Day 273**

**3,900  $\mu\text{g m}^{-2} \text{h}^{-1}$**

# Emission Rate Estimates for Various Ecosystems in the United States

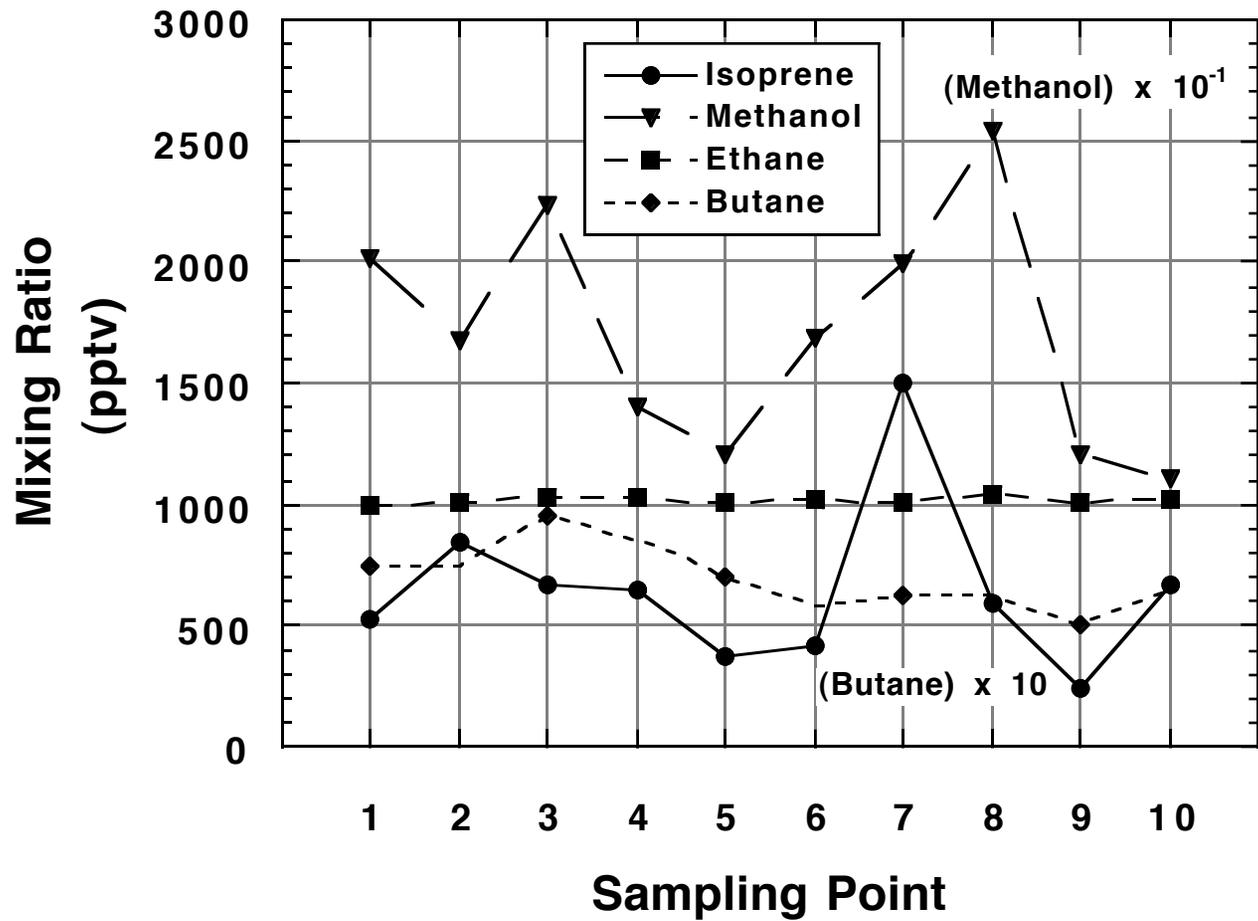
Ecosystem	Area, (10 <sup>6</sup> km <sup>2</sup> )	Emission Rate ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )				
		Isoprene	Monoterpenes	Methanol	Other NMOCs	Total NMOCs
Oak forests	0.749	6800	320	1300-4600	610	9100-12400
Deciduous forests	0.526	3200	520	610-3500	700	5000- 7900
Coniferous forests	1.216	1500	1700	680-2200	900	4800- 6300
Scrublands	1.564	1300	550	610-6100	650	3100- 8600
Grasslands	0.957	1100	390	620-1800	710	3100- 4300
Agricultural crops	1.595	29	110	-	310	-

# Modeling

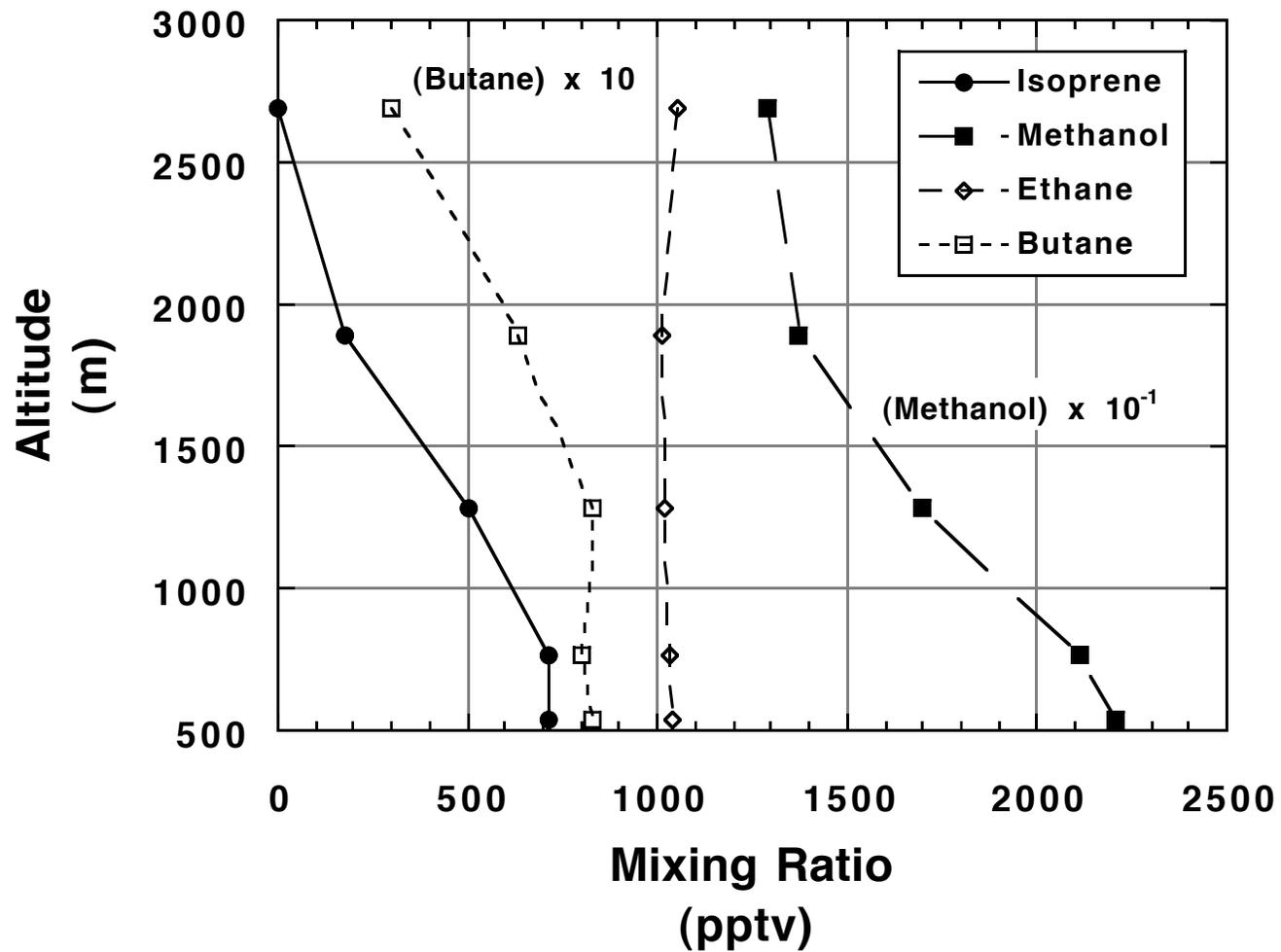
Whole air samples were collected in stainless steel canisters for NMOC analysis from aboard the **Battelle G-1 aircraft** along a transect and in vertical profiles above a forested region in Massachusetts during July of 1996 as part of ACP's participation in the North American Research Strategy for Tropospheric Ozone (**NARSTO**) Northeast 1996 Summer Ozone Study.

The **isoprene** concentrations at an altitude of 500 m varied from 0.4 to 1.5 ppbv along the transect and attained maximum levels above the Harvard Forest. Concentrations of **methanol** were 12-25 ppbv and covaried with isoprene. Isoprene and methanol concentrations above the Harvard Forest were 0.7 and 22 ppbv, respectively, at an altitude of 500 m; these concentrations decreased to 0.2 and 14 ppbv, respectively, at an altitude of 2000 m. In comparison, the concentration of **ethane**, a long-lived hydrocarbon of anthropogenic origin, was about 1 ppbv and invariant within the boundary layer. The levels of **n-butane**, a hydrocarbon originating from vehicle emissions, exhibited some horizontal variability and a vertical profile typical of a chemical species emitted from the surface.

# Transect

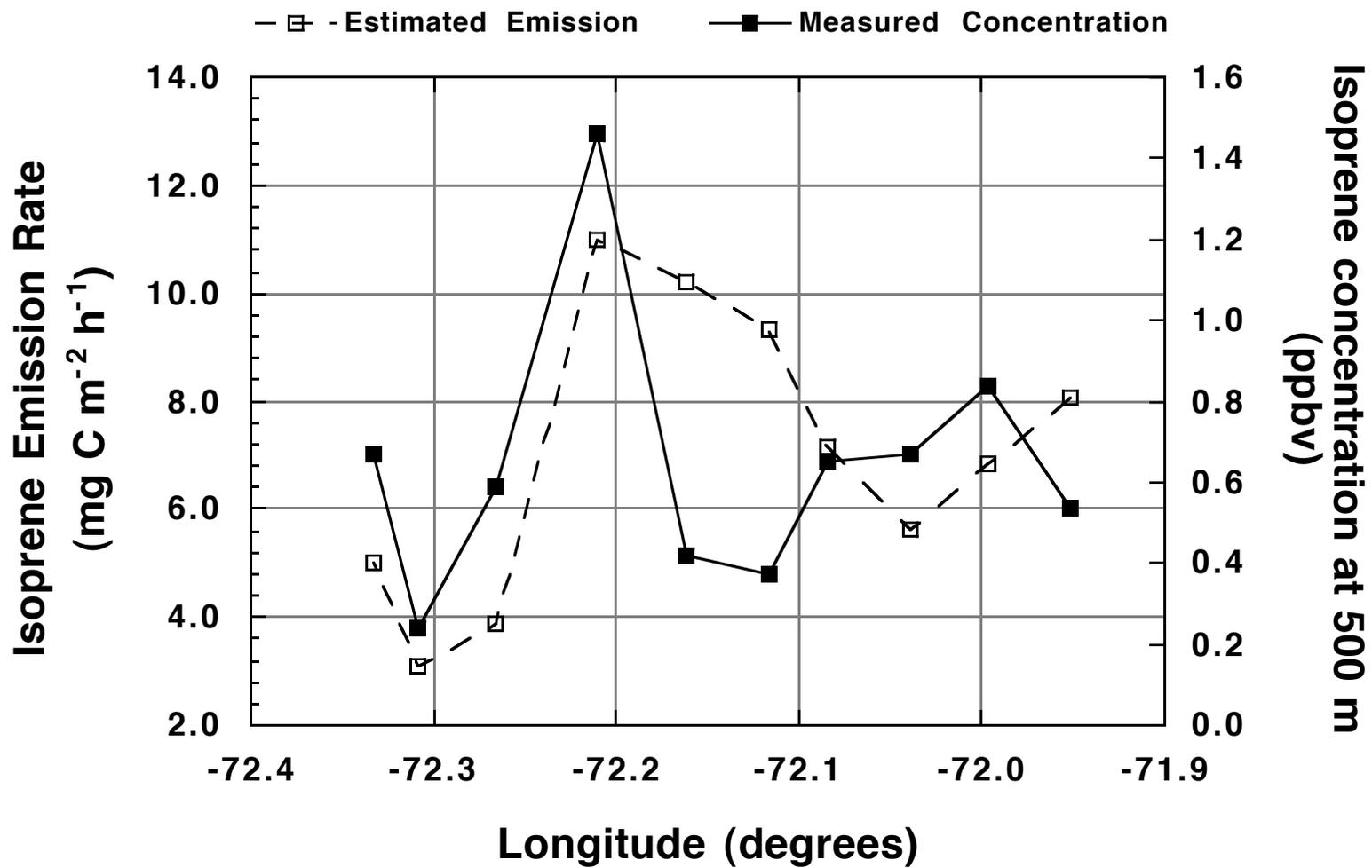


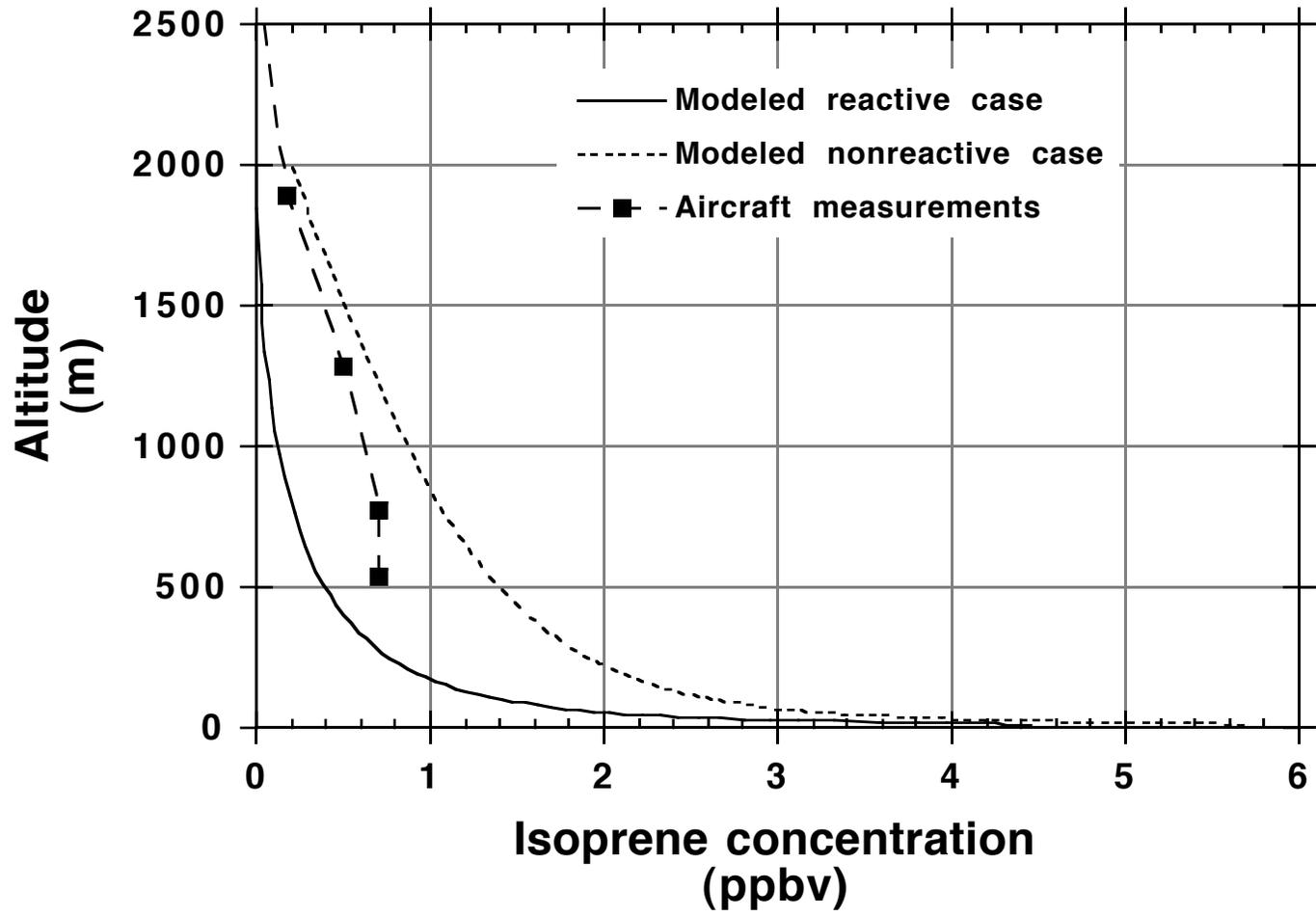
# Profile above Harvard Forest (Point 6)

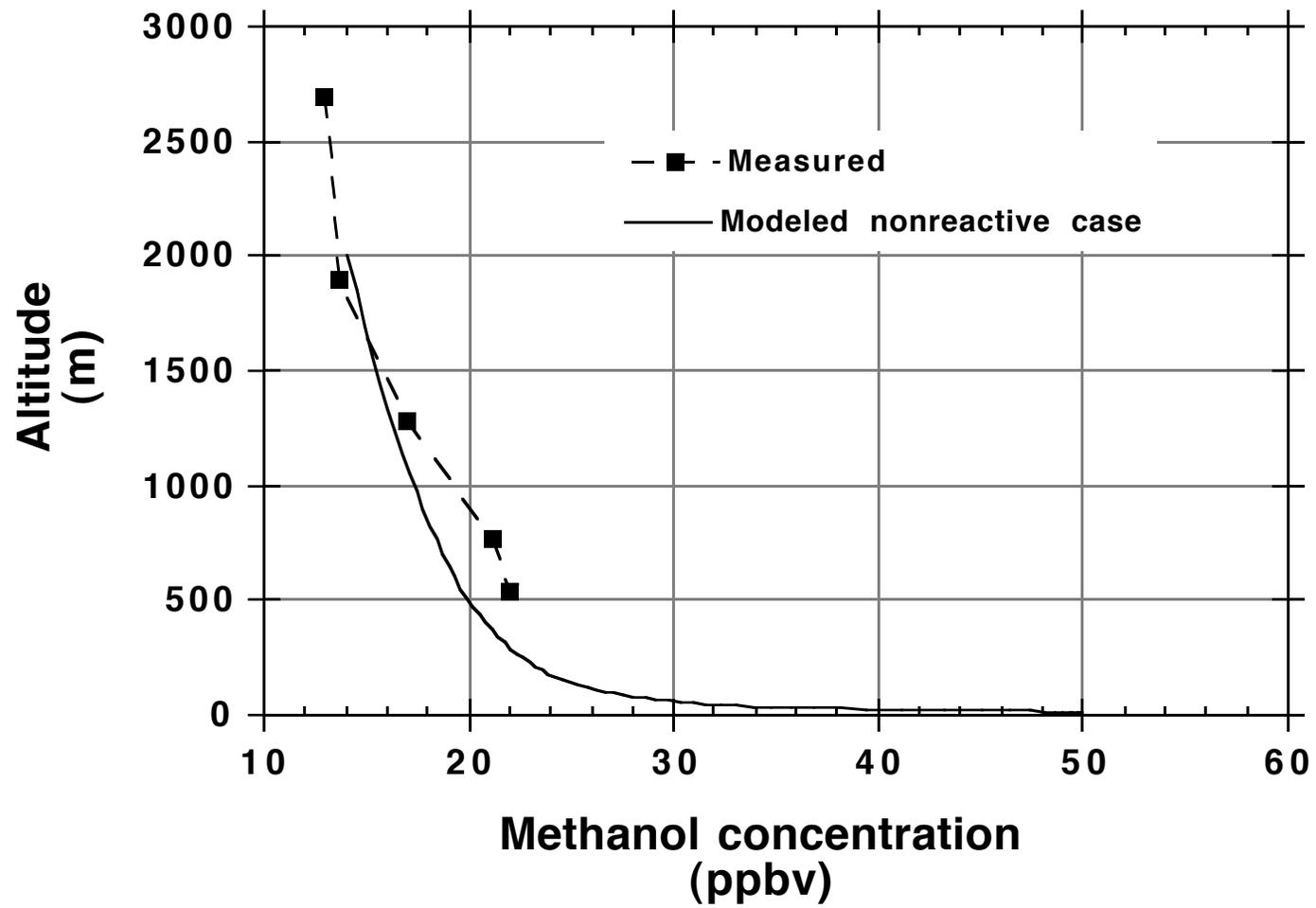


# The Transport-Chemistry Model

A **one-dimensional transport-chemistry model** was used to analyze the vertical profiles, which includes **parameterizations of biogenic emissions, dry deposition, chemical reactions** (69 in all), and turbulent transport for 34 reactive trace gases. The surface parameterizations for emission and dry deposition were driven by **satellite remote sensing data** to simulate the changes in biogenic emission of isoprene and dry deposition of various chemical species. In addition to the 45 reactions used to describe basic  $\text{NO}_x\text{-O}_3$  photochemistry, the model describes the reactions of isoprene and its oxidation products with  $\text{O}_3$  and  $\text{OH}$ . The photolysis rates within the canopy are adjusted to the decreasing radiation inside the canopy and are constant throughout the ABL above the canopy. The chemical reaction rates within the ABL are adjusted according to the measured temperature. The surface uptake of inorganic gases ( $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , etc.) by individual leaves is described in relation to stomatal functioning, which is regulated by PAR and air temperature. The biogenic emission of isoprene is described as a function of PAR and temperature within several layers of the forest canopy.







## Conclusions

Numerical simulations predicted low isoprene concentrations in the middle and upper ABL that were similar to the measured concentrations. Chemical oxidation of isoprene by  $O_3$  and OH, particularly in the middle and upper ABL, tends to reduce the isoprene concentrations and influences the vertical fluxes in that layer; however, chemical reactions have little effect on fluxes of isoprene near the emission source, where turbulent mixing is much faster than chemical reactions and where the emission process controls the vertical flux. The isoprene flux decreases rapidly with increasing height, with little isoprene escaping from the ABL. Vertical profiles of methanol concentrations were similar to the measured values for the well-mixed ABL but were much lower than the measured concentrations in the lower layers of the growing ABL because of weaker calculated mixing in the upper ABL during the morning. The results of this investigation indicate that chemical oxidation of isoprene is rapid enough to allow  $O_3$  and other oxidants to accumulate in the ABL on a regional scale if sufficient levels of nitrogen oxides are present; however, methanol is much more stable, and biogenic emissions of this compound have the potential to form  $O_3$  and other oxidants in areas distant from its source.

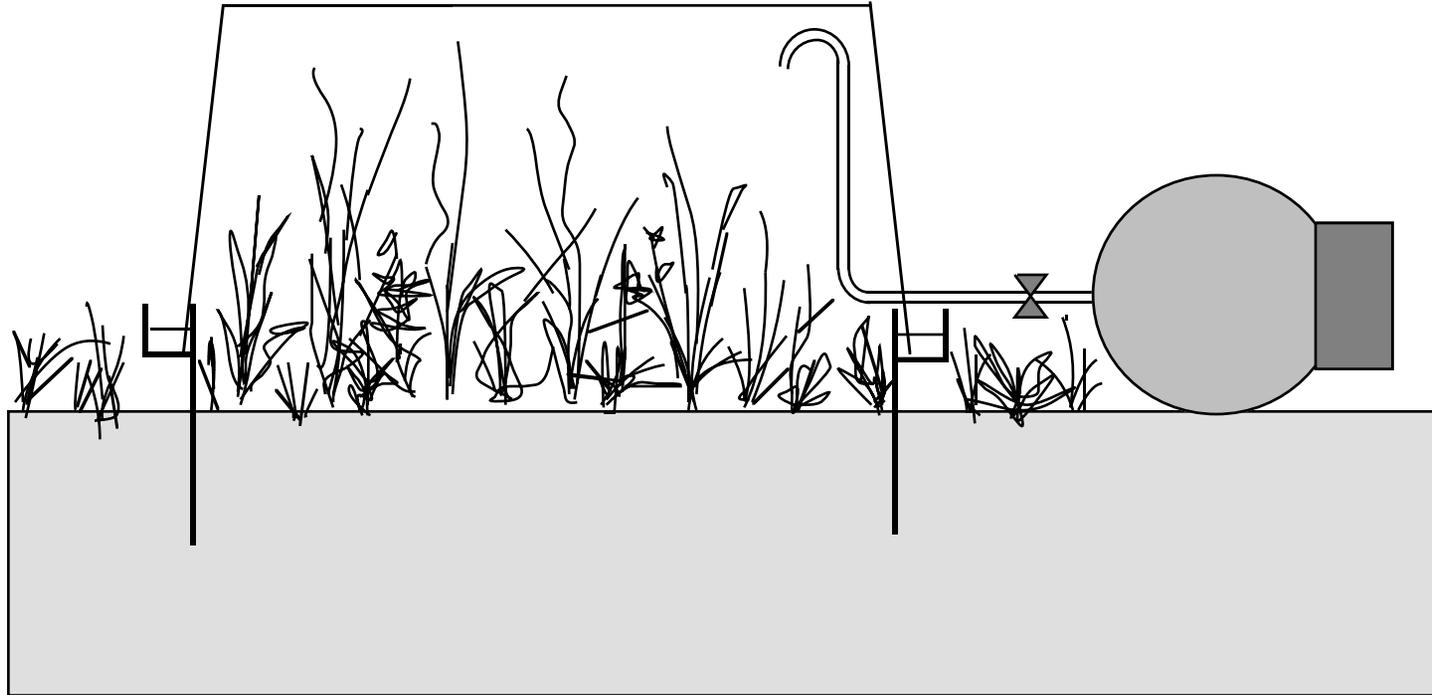
# **Instrument and Method Development**

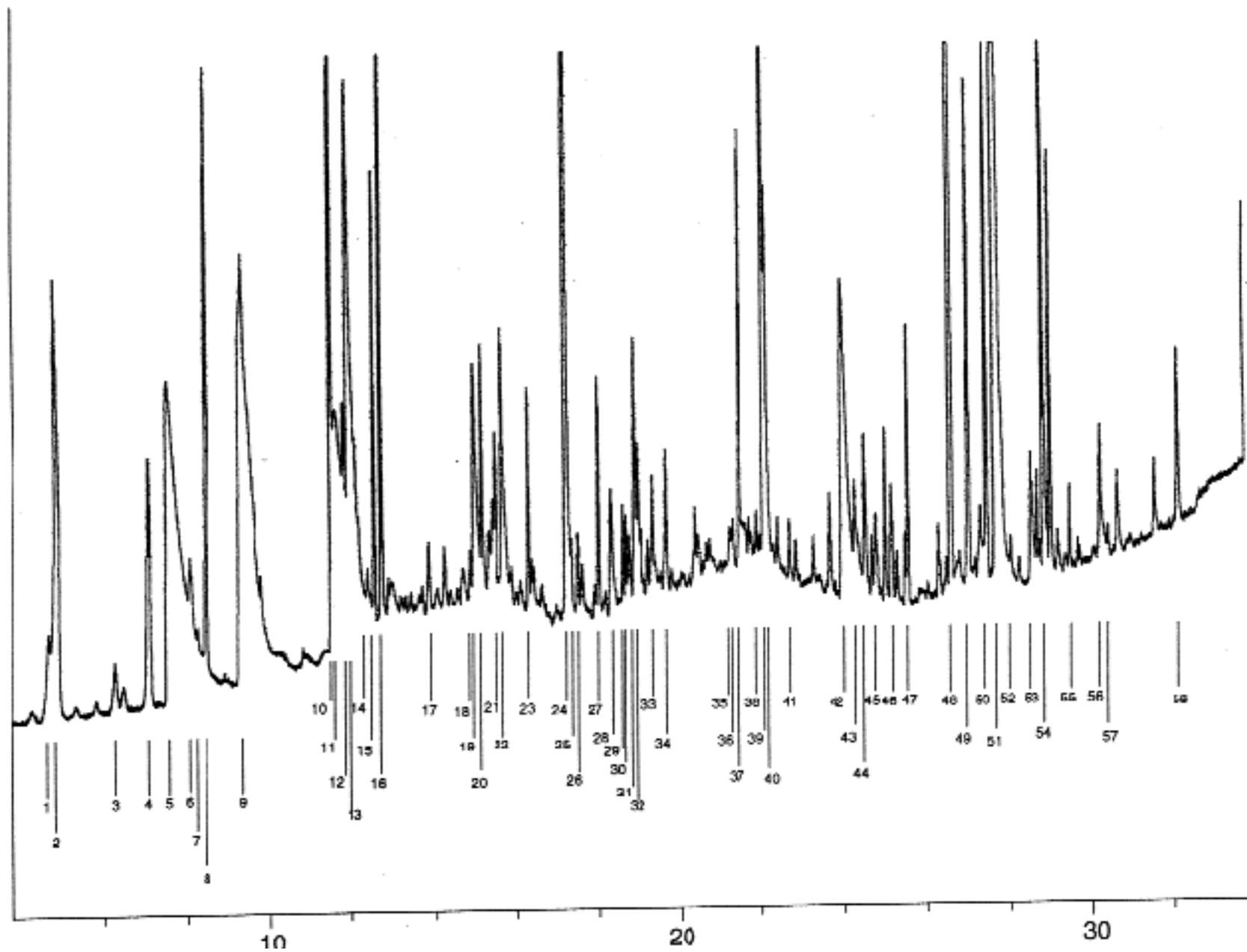
We have developed several sampling and analytic techniques for NMOCs. A common step of the analytic techniques is cryogenic preconcentration of the NMOCs on fused silica beads at  $-185^{\circ}\text{C}$ . The **static chamber sampling method** was developed to measure NMOC emissions from grassland vegetation. Whole-air samples are preconcentrated without removing water so that the **OxHCs** are not lost.

The **evacuated chamber method** was developed to collect whole-air samples for the analysis of organic nitrates. The sample is collected in a Tedlar<sup>®</sup> bag by withdrawing air from the stainless steel chamber. This technique is well suited to the thermally labile, **peroxyacyl nitrates** because the sample does not go through a pump before it enters the sample container.

A high-resolution gas chromatograph was developed to perform **in situ** NMOC analysis from aboard an aircraft. The ambient air sample enters directly into a cryogenic trap and is analyzed for **C<sub>2</sub>-C<sub>6</sub> NMHCs** (approximately 40 hydrocarbons) in 9 min. A distinct advantage of the **aircraft gas chromatograph** is its ability to take the sample directly into the instrument.

# Static Chamber Sampling Method

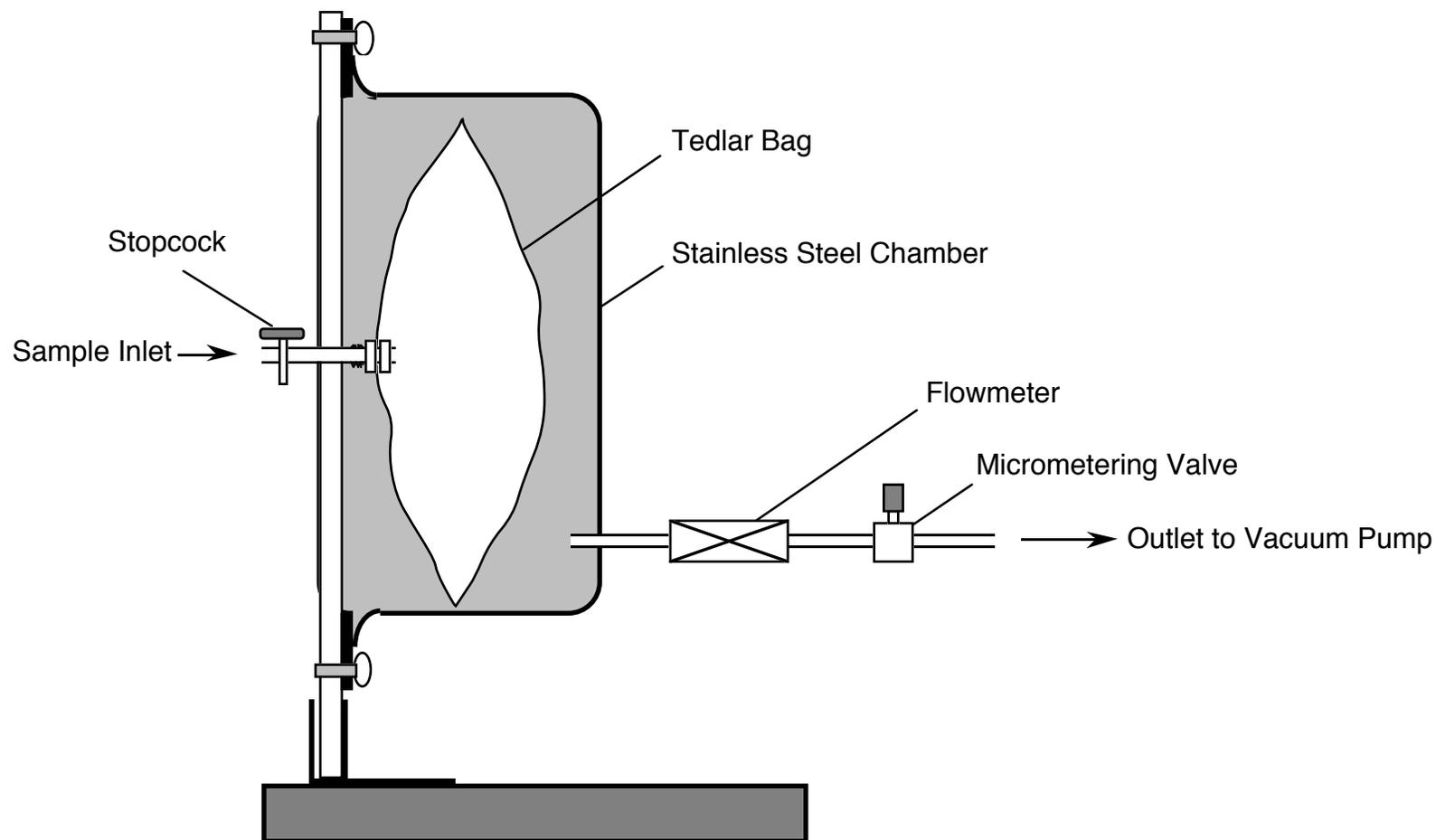




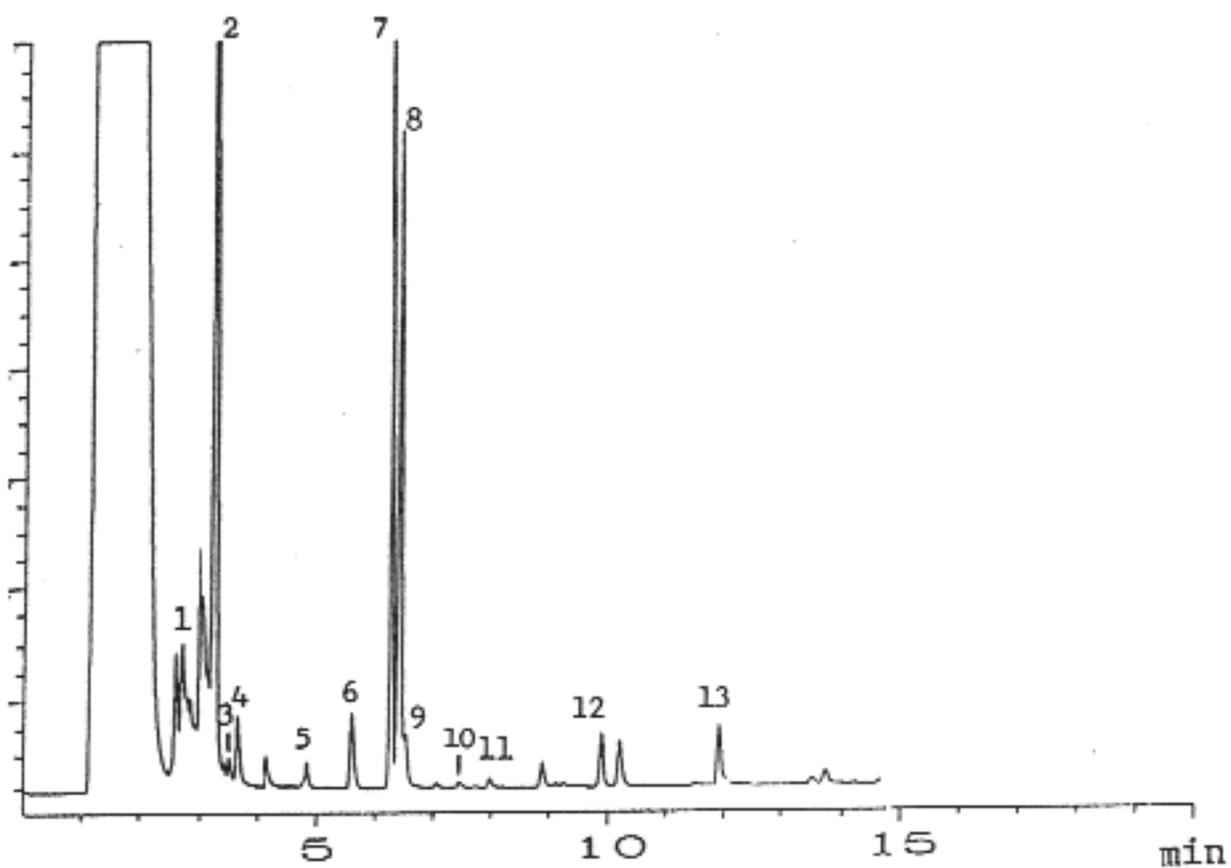
**Tentative identifications and retention times for the NMOs  
in the high-resolution gas chromatogram.**

Key	Time min	Compound	Key	Time min	Compound
1	5.101	Propene	30	19.275	2,3-Dimethylpentane
2	5.274	Propane	31	19.491	2- and 3-Methylhexane/ 3-Pentanone
3	6.740	Chloromethane	32	19.565	Pentanal
4	7.547	2-Methylpropane	33	19.953	2,2,4-Trimethylpentane
5	8.066	Ethanal	34	20.272	Heptane
6	8.566	2-Methylpropene	35	21.836	1-Pentanol
7	8.574	1-Butene	36	21.912	2,3,4-Trimethylpentane
8	8.967	Butane	37	22.093	Toluene
9	9.864	Methanol	38	22.512	2-Hexanone
10	12.028	2-Methylbutane	39	22.684	<i>trans</i> -2-Hexen-1-al
11	12.130	Ethanol	40	22.758	Hexanal
12	12.329	Propanal	41	23.345	Octane
13	12.415	Acetone	42	24.636	<i>cis</i> -3-Hexen-1-ol
14	12.928	2-Methyl-1-butene/ 2-Propanol	43	24.918	Ethylbenzene/1-Hexanol
15	13.086	Pentane	44	25.150	<i>m</i> - and <i>p</i> -Xylene‡
16	13.253	Isoprene	45	25.413	2-Heptanone
17	14.425	2,2-Dimethylbutane	46	25.825	<i>o</i> -Xylene‡
18	15.456	4-Methyl-1-pentene	47	26.149	Nonane
19	15.557	1-Propanol	48	27.272	$\alpha$ -Pinene
20	15.738	2-Methylpentane	49	27.691	1-Heptanol
21	16.058	Butanal	50	28.159	$\beta$ -Pinene
22	16.252	2-Butanone	51	28.389	Myrcene/Octanal/ <i>cis</i> -3-Hexenylacetate
23	16.875	Hexane	52	28.724	Decane
24	17.889	Methylcyclopentane†	53	29.217	$\Delta^3$ -Carene/ $\alpha$ -Hydroxytoluene
25	17.933	2,4-Dimethylpentane	54	29.540	Limonene
26	18.089	1,1,1-Trichloroethane	55	30.160	1-Octanol
27	18.630	Benzene	56	30.918	Nonanal
28	18.930	1-Butanol	57	31.105	Undecane
29	19.203	Cyclohexene	58	32.814	1-Nonanol

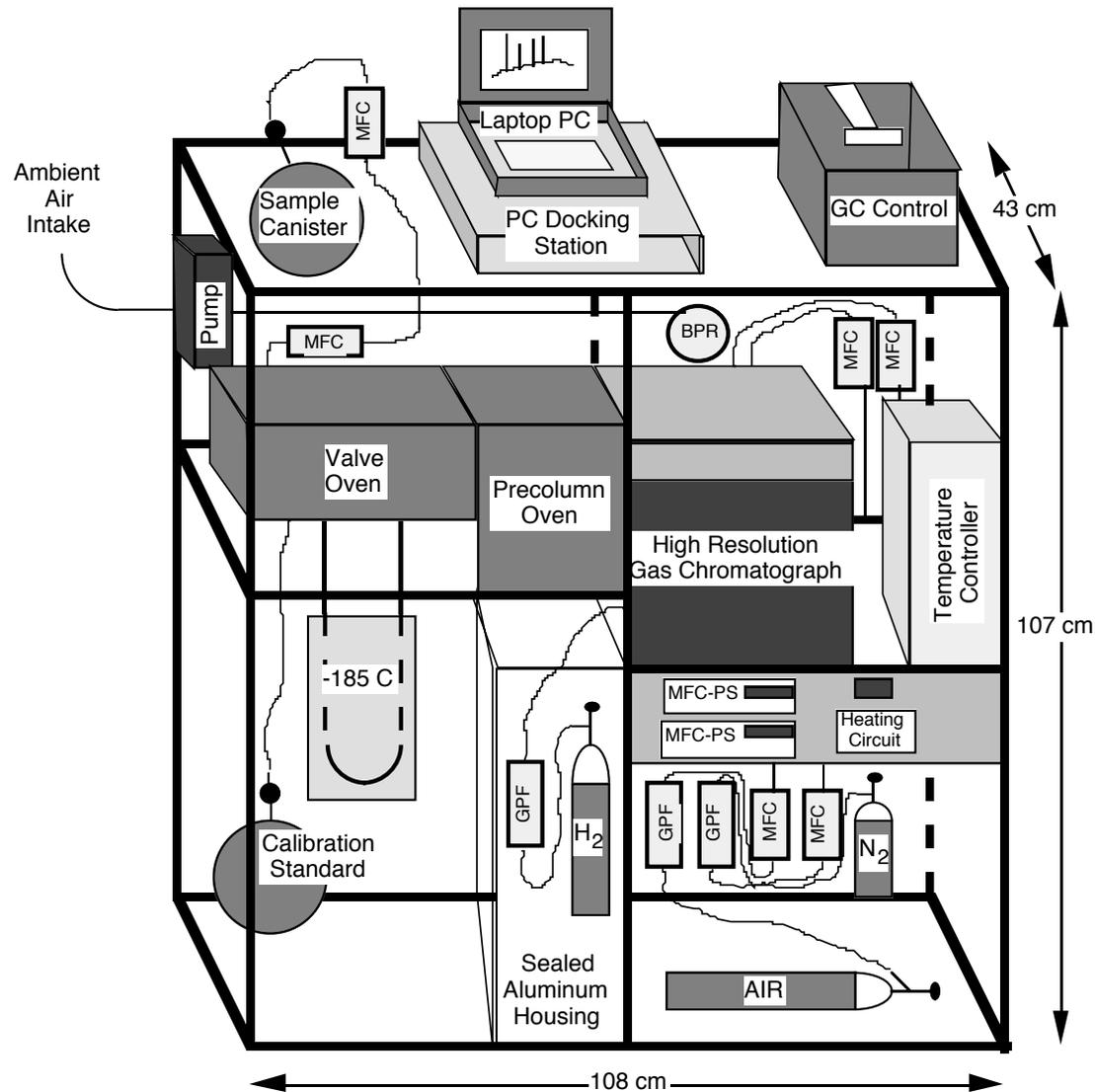
# Evacuated Chamber Sampling Method



High-resolution gas chromatogram of an ambient-air sample collected by the evacuated chamber method. Peak identification: 1, Freon 12; 2, Freon 11; 3, dichloromethane/methyl nitrate; 4, Freon 113; 5, trichloromethane/ethyl nitrate; 6, 1,1,1-trichloroethane; 7, carbon tetrachloride; 8, PAN; 9, 2-propyl nitrate; 10, trichloroethylene; 11, *n*-propyl nitrate; 12, PPN; and 13, tetrachloroethylene/PBN.



# Aircraft Gas Chromatograph



GPF, Compressed gas purifier  
MFC, Mass flow controller  
MFC-PS, Mass flow controller power supply

# Features

- Simultaneous Sampling into Canister and Gas Chromatograph
- Ozone Removal prior to Hydrocarbon Preconcentration
- Cryogenic Preconcentration
- High Resolution Gas Chromatography
- Flame Ionization Detection
- Data Acquisition

# Capabilities

- C<sub>2</sub>-C<sub>6</sub> NMHCs

- Detection Limit - 10 pptC

- Sampling and Analysis Cycle - 14 min

Sampling and Cryogenic Preconcentration	5 min
---	-------

Thermal Desorption	2 min
--------------------	-------

Cryogenic Trap Cooling	5 min
------------------------	-------

Gas Chromatographic Analysis	9 min
------------------------------	-------

Gas Chromatograph Oven Cooling	5 min
--------------------------------	-------